

# Exact solution of the Percus-Yevick integral equation for “collapsing” hard spheres

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By Wertheim-method the exact solution of the Percus-Yevick integral equation for a system of particles with the “repulsive step potential” interacting (“collapsing” hard spheres) is obtained. On the basis of this solution the state equation for the “repulsive step potential” is built and determined, that the Percus-Yevick equation does not show phase transition for “collapsing” hard spheres.

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In 1963 Wertheim and Thiele independently gained the exact analytical solution of the Percus-Yevick integral equation for hard spheres [1]-[3]. This solution is so far the only strict analytical one of non-linear integral equation for pair distribution function. The given work shows the possibility of Wertheim method to express the solution of the Percus-Yevick equation in closed analytical form for more complicated particles interaction potential — repulsive step potential [4]

$$V(r) = \begin{cases} \infty, & r < a \\ V_0, & a \leq r \leq b \\ 0, & r > b. \end{cases} \quad (1)$$

where  $V_0$  — positive constant,  $r$  — particles range (“collapsing” hard spheres).

Such a potential used to have a great application in modeling phase transition in liquid under the high pressure, isostructural phase transitions in crystals, transformations in colloid systems, etc. by means of molecular dynamics within the framework of thermodynamic perturbation theory [4, 5].

Let’s consider the Percus-Yevick equation

$$n_2(r) = 1 - n \int [e^{\beta V(\vec{s})} - 1] n_2(\vec{s}) \times \quad (2) \\ \times [n_2(\vec{r} - \vec{s}) - 1] d\vec{s}$$

where  $n_2(r)$  — the pair distribution function,  $\beta = \frac{1}{kT}$ ,  $n$  — the particle density. Moving to bipolar coordinates and integrating for angle variable for the “repulsive step potential” we gain that

$$h(r) = Ar - 2\pi n \int_0^a h(s) ds \int_{|r-s|}^{r+s} h(t) e^{-\beta V(t)} dt - \quad (3) \\ - 2\pi n (1 - e^{-\beta V_0}) \int_a^b h(s) ds \int_{|r-s|}^{r+s} h(t) e^{-\beta V(t)} dt$$

where

$$h(r) = r n_2(r) e^{\beta V(r)} = \begin{cases} -rC(r), & r < a \\ \frac{-rC(r)}{1 - e^{-\beta V_0}}, & a \leq r \leq b \\ n_2(r), & r > b \end{cases} \quad (4)$$

$C(r)$  — direct correlation function. In the approach of Percus-Yevick

$$C(r) = (1 - e^{\beta V(r)}) n_2(r)$$

$n_2(r) = 0$  at  $r < a$ ,  $C(r) = 0$  at  $r > b$ , and  $e^{-\beta V(t)} = e^{-\beta V_0} \Theta(t - a) \Theta(b - t) + \Theta(t - b)$ ;

$\Theta(x)$  — Haviside step function;

$$A = 1 + 4\pi n \int_0^a h(s) ds + 4\pi n(1 - e^{-\beta V_0}) \int_a^b h(s) ds$$

We take the one-side Laplace transform for (3)  $\hat{L}(h(r)) = \int_0^\infty h(r)e^{-zr} dr$  and change the order of integration for  $r$  and  $t$ , we finally obtain:

$$\psi(z) = \frac{\frac{A + \gamma z \delta(z)}{z^2} - L(z)}{1 - \frac{2\pi n}{z} [L(z) - L(-z)]} \quad (5)$$

where

$$\begin{aligned} \psi(z) &= \hat{L}(rn_2(r)) = G(z) + e^{-\beta V_0} K(z) \\ L(z) &= \hat{L}(-rC(r)) = F(z) + (1 - e^{-\beta V_0}) K(z) \\ F(z) &= \int_0^a h(s) e^{-zs} ds \\ K(z) &= \int_a^b h(s) e^{-zs} ds \\ G(z) &= \int_b^\infty h(s) e^{-zs} ds \\ \delta(z) &= \alpha(z) - \alpha(-z) \\ \gamma &= 2\pi n e^{-\beta V_0} (1 - e^{-\beta V_0}) \end{aligned}$$

For further investigation we lead in the following function

$$H(z) = z^4 \psi(z) \left[ \frac{A + \gamma z \delta(z)}{z^2} - L(-z) \right] \quad (6)$$

Discussions like in [2] show that

$$H(z) = \lambda_1 + \lambda_2 z^2,$$

where  $\lambda_1, \lambda_2$  — are constants. Not including  $\psi(z)L(-z)$  from (5) and (6) and turning the Laplace transform into the  $r \leq b$  area, we gain the explicit expression for  $h(r)$

$$h(r) = -(C_0 + C_1 r + C_2 r^2 + C_3 r^4) \quad (7)$$

where

$$\begin{aligned} C_0 &= 2\pi n e^{-\beta V_0} (\lambda_1 k_2 + k_0 (\gamma \delta_1 - l_0)) \\ C_1 &= \lambda_1 (-1 + 2\pi n e^{-\beta V_0} k_1) \\ C_2 &= \pi n (-\lambda_2 + \lambda_1 k_0 e^{-\beta V_0}) \\ C_3 &= -\frac{\pi n \lambda_1}{12} \end{aligned}$$

and the constants  $\lambda_1, \lambda_2, k_0, k_1, k_2, l_0$  and  $\delta_1$  as density, temperature and potential parameters  $V_0, a, b$  functions can be obtained from the system of equations

$$\begin{aligned} \lambda_1 &= A = 1 + 4\pi n \int_0^a r h(r) dr - 4\pi n (1 - e^{-\beta V_0}) k_1 \\ \lambda_2 &= 2\gamma \delta_1 - 2l_0 - \frac{2\pi n}{3} \times \\ &\times \left[ \int_0^a r^3 h(r) dr + (1 - e^{-\beta V_0}) \int_a^b r^3 h(r) dr \right] \\ k_m &= \frac{(-1)^m}{m!} \int_a^b r^m h(r) dr, \quad m = 0, 1, 2, \\ l_0 &= \int_0^a h(r) dr + (1 - e^{-\beta V_0}) k_0 \\ \delta_1 &= \int_a^b \int_s^b h(s) h(t) (t - s) dt ds \end{aligned} \quad (8)$$

Inserting (7) into (5), we gain the Laplace image form for  $rn_2(r)$ .

The system of “collapsing” hard spheres state equation can be shown as

$$\begin{aligned} \frac{P}{nkT} &= 1 - \frac{n}{6kT} \int rn_2(r) \left( \frac{dV}{dr} \right) \vec{dr} = \\ &= 1 + \frac{2\pi n}{3} [e^{-\beta V_0} a^3 \tau(a) + (1 - e^{-\beta V_0}) b^3 \tau(b)] \end{aligned} \quad (9)$$

where  $\tau(r) = h(r)r^{-1}$  and inverse isothermic compressibility

$$\begin{aligned} \left( \frac{\partial P}{\partial n} \right)_T \frac{1}{kT} &= \\ &= 1 - n \int C(r) \vec{dr} = \lambda_1(n, T) \end{aligned} \quad (10)$$

It can be seen from (10) and (8) that if  $V_0 > 0$

$$\left(\frac{\partial P}{\partial n}\right)_T > 0 \quad (11)$$

i.e. the Van der Waals loop is absent in the isotherm. This result coincides with those ones which were taken in numerical analysis of the state equation (9).

Thus, the Percus-Yevick equation for the system of “collapsing” hard spheres allow the solution in closed analytical form going into the Wertheim-Thiele classical solution for hard spheres when  $a = b$ . As in the case of hard spheres the Percus-Yevick solution doesn't show the phase transition in the system of “collapsing” hard spheres.

## References

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